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TITLE: HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE PYROLYSIS TREATMENT AND HALOGENATION OF MULTI-ELEMENT WASTE

INVENTOR(S) Ariel ROSENBERG
7 Hazav Street
84965 Omer, Israel

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אני, (שם המבקש, מענו ולגבי גוף מאוגד - מקום התאגדותו)
I, (Name and address of applicant, and in case of body corporate-place of incorporation)

Ariel ROSENBERG אריאל רוזנברג
7 Hazav Street רח' חצב 7
Omer עומר

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(בעברית) (Hebrew) תהליך בעל יעילות גבוהה למיחזור פסולת רב-מרכיבית

(באנגלית) (English) HIGH EFFICIENCY RECOVERY PROCESS OF MULTI-ELEMENT WASTE

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תהליך בעל יעילות גבוהה למיחזור פסולת רב-מרכיבית

HIGH EFFICIENCY RECOVERY PROCESS OF MULTI-ELEMENT WASTE

HIGH EFFICIENCY RECOVERY PROCESS OF MULTI-ELEMENT WASTE

FIELD OF THE INVENTION

The field of the present invention is processes for treating and recovering a large variety of types of wastes via chemical treatment.

BACKGROUND OF THE INVENTION

The present recovery and recycling industry must use a defined feed stock as raw material in order to be processed. As a result, the recovery industry must spend huge resources in sorting its wastes storing and warehousing. This is the main reason for the small quantity of waste which is actually being recycled, and the huge amount which is being dumped with catastrophic environmental effects.

Examples of the above are known and obvious, such as special scrap collectors, scrap yard dealers, for each segment of the industry - copper, aluminum, iron, steel, stainless steel, noble metal etc. in the recycling industry on the one hand, and the unlimited amount of waste being dumped by the society every day, on the other hand

However, the recycling industry is dedicated mainly to the industrial waste, which is well sorted and defined to each element. In the event that

the scrap is made of different elements or metals, cheap labor is needed in order to dismantle the different components to the different metals. Examples are found in ship scrap, aircraft, cars and municipal waste. The main problem is, that this process requires cheap manpower that have to work in difficult and hazardous conditions. It has been proven in the developed countries, that manual or automated sorting and dismantling systems are usually not economically feasible and are therefore not a valid solution for treatment of most of the mixed waste.

Indeed many industries do address this issue by constructing equipment which makes recycling easy by use of the dismantling methods, such as used in the automobile industry etc. However, due to the use of many complex materials and the sophistication of parts it becomes almost impossible to re-use these parts or repair them.

The only system that treats unsorted waste, to any degree is the Municipal Incineration system, and even then, the waste must not be contaminated by industrial or Hazardous waste. In this system the waste is being introduced into furnaces and incinerated at elevated temperatures, where hot gases usually produce steam and or electricity. This system actually recovers only the energy of the organic matter via oxidation - incineration. All the inorganic waste remains as ash or sludge and is usually placed in a controlled landfill.

There are some other systems that have been developed to recover identified elements from identified feed stock - waste, via different systems, such as molten metals, extraction or chlorination methods. For example, Adelman et al. (Proc. Iowa Acad. Sci. (1980) 87 (4), pp129-133) discloses the production of aluminum chloride and silicon chloride from fly ash. In this system recovery of Al, Si, Fe, and Ti via chlorination reaction in a gas fluidized bed reactor is used, to convert the metal in the fly ash to volatile metal chlorides. The best yields are achieved when CO and fluid coke are used as reduction agents. Typically 0.5 - 2 hours of chlorination at temperatures of 750 - 900 degrees to produce volatile metal chlorides.

Burnet et al. (Univ. Ky., Inst. Min. Miner. Res., [Tech Rep.] IMMR (1997), IMMR 32-M4-77, Proc. - Ky. Coal Refuse Disposal Util. Semin., 3rd 83-8) discloses a high temperature chlorination method of recovering Al_2O_3 from the non-magnetic fraction of fly ash, in which the non-magnetic fraction of fly ash is mixed with C and chlorinated in a fixed bed. The residual Fe in the ash can be removed as volatile Fe chloride at 400-600°C, with very little Al and Si reaction. The temperature is than raised to 850-950°C where a mixture consisting mostly of volatile Al and Si chloride forms. When the vapors are cooled, solid $AlCl_3$ condenses at 120-50°C. The $SiCl_4$ remains in a vapor state due to its low condensation temp. The $SiCl_4$ can

be easily decompounded to form SiO_2 and HCl from which the Cl is recycled.

Most wastes contain more than one element and several unknown contaminates. Most wastes contain both organic and non-organic elements.

The organic waste materials are in most cases a mixture of various chains of molecules together with various elements incorporated, as well as other non-organic materials, and are usually difficult in recycling, and they create environmental problems.

Chlorination of organic material can produce hazardous, toxic and cancerous elements.

It is a purpose of the present invention to provide a process for destruction of hazardous and/or toxic industrial waste in which the toxic and/or the hazardous compound waste is reduced into less toxic, or non toxic material, and/or less hazardous or non hazardous material, and the size and quantity of said waste is also reduced.

It is a further purpose of the present invention to provide a self-catalytic process in which the matter that exists in the compounded waste is converted and used as a catalyst in a subsequent reaction.

It is a further purpose of the present invention to provide an energy recycling process in which the energy produced by one chemical reaction is consumed in a subsequent chemical reaction.

It is a further purpose of the present invention to provide a wide range recycling process in which almost any waste can be treated: organic, non-organic, metallic or non-metallic, sorted or even unsorted.

It is a further purpose of the present invention to provide a recycling process suitable for recovering the basic elements of the waste introduced thereto, thus obtaining valuable and useful materials.

SUMMARY OF THE INVENTION

The present invention relates to a high efficient recovery process for the treatment of multi-element wastes which comprises the steps of:

a) heat treatment of the waste in the presence of a controlled amount of oxygen;

b) halogenation of the product of step "a"; and

c) separation of the metal halide products of step "b".

The term “carbonization” used herein is defined as an operation in which organic material is subjected to high temperature in the presence of a limited amount of oxygen, resulting in the decomposition of said material, and affording, *inter alia*, carbon, CO and CO_2.

The heat treatment described in the above step “a” may be referred to hereinafter as “primary heat treatment”.

Optionally, when necessary, the raw waste is mechanically prepared in a process which includes any of the steps of shredding, crushing, milling and briquetting, prior the step of primary heat treatment.

Preferably the primary heat treatment is performed at a temperature of less than about 1000^{o}C.

Preferably, during the primary heat treatment, the waste is agitated.

Preferably, the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

Preferably, the halogenation reaction is conducted with mechanical movement between the gaseous halogen and the waste, as fixed fluidized bed vibrating or in walking grid.

Preferably, the halogenation reaction is a chlorination reaction, a bromination reaction or a combined chlorination-bromination reaction, and more preferably a chlorination reaction.

Preferably, the halogenation reaction is performed at a temperature of between 150°C and 1500°C, more preferably between 700 °C and 750 °C.

Optionally, the halogenation temperature may vary according to the boiling or sublimation point of the metal halide products.

Preferably, the separation of the halide products (step "c" above) is by means of any one or more, or any combination of operations selected from the group consisting of gaseous or liquid fractional deposition, distillation, filtration, settling, selective oxidation, selective halogenation, selective dissolution and selective extraction, and more preferably by means of gaseous fractional deposition.

Optionally, a portion of the heat energy posessed by the product material of the primary heat treatment may be used in the halogenation, e.g., said

product of the primary heat treatment may be transferred from the primary heat treatment chamber to the halogenation chamber when hot, and the halogenation reaction may be started shortly afterwards, and thus it is required to heat the material of the halogenation reaction merely from the temperature which it is at, and is substantially higher than, e.g., room temperature.

Optionally, the activation of metals in the halogenation reaction may be catalyzed by the introduction of the carbon produced during the primary heat treatment and/or of untreated flu-gas including e.g. bromine, carbon, CO, CO_2 and SO_x and NO_x compounds from the primary heat treatment chamber into the halogenation chamber.

The present invention further relates to an apparatus by which such a recovery process is performed, which comprises a primary heat treatment chamber, a halogenation chamber and a separation unit; said primary heat treatment chamber comprises a waste inlet, a flu-gas outlet and means of heating, and is preferably connected to said halogenation chamber by means of a conduit, which comprises a valve; and said halogenation chamber comprises a means of controlled heating, a halogen compound inlet and optionally an outlet; said apparatus further comprises a separation system comprises one or more of the following units, or any combination thereof, selected from the group consisting of fractional

deposition unit, distiller, filter, settler, selective oxidation chamber, selective dissolution unit and selective halogenation system; said unit or units optionally being in contact with the outlet of said halogenator by means of a conduit.

Preferably, said separation system is a gaseous fractional deposition system and is connected to the outlet of said halogenator, by means of a conduit.

Preferably, said fractional deposition system comprises one or more deposition columns wherein each column comprises means of maintaining the temperature thereof at a pre-determined level; said fractional deposition system further comprising an outlet pipe.

Preferably, said outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber.

Optionally, said apparatus further comprises on or more units which can perform one or more actions selected from any of the group which consists of shredding, crushing, milling and briquetting, or any combination thereof, said units being connected to the inlet of said primary heat treatment chamber and/or to the inlet or said halogenation chamber by means of a conduit.

Preferably, said apparatus further comprises an additional heat chamber, referred to hereinafter as secondary heat chamber, a heat exchanger, a scrubber, a filter, a blower and a stack; said additional heat chamber comprising a means of heating, a gas inlet and an air inlet, and a flu gas outlet; said gas inlet of said secondary heat chamber being connected by means of a conduit to the flu gas outlet of said primary heat chamber; said heat exchanger comprising an inlet and an outlet; the flu gas outlet of said secondary heat chamber being connected by means of a conduit to the inlet of said heat exchanger; said scrubber comprising an inlet and an outlet; the outlet of said heat exchanger being connected, by means of a conduit to the inlet of said scrubber;

Preferably, said apparatus further comprises a filter, a blower and a stack; said filter comprising an inlet and an outlet; the outlet of said scrubber being connected, by means of a conduit to the inlet of said filter; said blower comprising an inlet and an outlet; the outlet of said filter being connected, by means of a conduit to the inlet of said blower; said stack comprising an inlet and an outlet; the outlet of said blower being connected, by means of a conduit to the inlet of said stack;

DESCRIPTION OF THE INVENTION

The present invention relates to a high efficient process for the treatment of wastes which is applicable in treating mixtures of waste. Said mixtures consisting of a very wide range of chemical elements and compounds, organic and non-organic, in different physical forms, such as solid, liquid and gas. Said process comprises the following steps:

a) Primary heat treatment of the waste:

Said stage optionally includes evaporation of water, evaporation and carbonization of organic matters from the waste in a controlled oxygen atmosphere preferably at a temperature of less than 1000°C, or in metallic molten bath, said bath preferably being at a temperature of between 500°C and 1600°C. In the presence of hazardous waste, a secondary combustion chamber will destroy all remaining organic matters in the flu gas at a temperature of more than 1200°C at minimum of 2 seconds retention time. The primary heat treatment is conducted at a controlled oxygen level, thus, it may produce controlled and reduced metallic oxides and exchange or reduce the oxygen layer with carbon, and produce carbon residue which acts both as a catalyst in the halogenation reaction and impregnates into a portion the metal phase at elevated temperature which all will facilitate the halogenation reaction.

b) Halogenation of the product of the heat treatment:

Material present in the remainder of the waste which may include metals, metal carbides, metal oxides, other inorganic material and possibly traces of organic material is halogenated at a temperature between 300°C and 1500°C, preferably between 700°C and 750°C. The carbon remaining in the waste, together with additional carbon, if required, acts as a catalyst in the halogenation. Preferably, the halogenation reaction is a chlorination reaction, a bromination reaction or a combined chlorination-bromination reaction, and more preferably the halogenation reaction is a chlorination reaction. Preferably, all of the above halogenation reactions are preformed in the gaseous phase.

The halogenation reaction may be conducted with various mechanical apparatus such as fluidized bed, vibrating grid, walking grid or multi chamber.

The primary heat treatment chamber and/or the halogenation chamber of the present invention may each independantly be placed horizontally, vertically or in an angle.

The halogenation reaction may be conducted at a temperature suitable for causing the products to separate due to the differences of their phase

transition temperatures, e.g., at a temperature in which one or more products is/are a gas, and on or more other products is/are liquid or solid.

c) Separation of the halide products: such a separation can be done by means of any one or more, or any combination of separations selected from the group consisting of gaseous or liquid fractional deposition, distillation, filtration, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution and selective extraction, and more preferably by means of gaseous fractional deposition (see, e.g. Zelickman A.N. Nikitina L.L. Moscow 1978).

Gaseous fractional deposition may be performed passing all the volatile chlorides, M_xCl_y, through one or more solidifying columns. Each has a temperature controlled system that maintains accurate conditions of e.g. temperature. The halide with the highest solidifying temperature solidifies in the first column, whereas the remainder of the halides in the gaseous phase pass to the next columns for further solidifying. In each solidifying column, there will be one or more definite halide materials. The resolution of the separation depends on the accuracy of the solidifying temperature and pressure control, and the dynamics of the gaseous flow. The solidified halides of each column may consist of the solidifying of several halides which are further separated and purified by known

technologies of hydrometallurgy, such as solution in water or other liquids and filtration (see, e.g. Zelickman A.N. Nikitina L.L. Moscow 1978)

The halides in the reactor which are at higher volatile temperatures are left together with the residues which were not halogenated such as glass and ceramics. The mixed material is removed from the bottom of the reactor to be further treated by e.g. a high temperature halogenation reactor which reaches 900-1500 degrees or by known hydrometallurgy technologies (see, e.g. Zelickman A.N. Nikitina L.L. Moscow 1978).

Optionally, the raw waste and/or the product of the primary heat treatment is mechanically prepared in a process which includes any one or more of the following steps:

i) mechanical shaping of solid waste into pieces of a size to suit further equipment and productivity.

ii) crushing and/or milling of waste;

iii) briquetting of sludge

According to one embodiment of the present invention, a mixture of 1%-7% bromine in chlorine is used in the halogenation stage in the event that noble metal atoms or compounds such as Ag, Pt and Pd are present.

It is preferable to execute the primary heat treatment at a low as possible temperature in order to substantially reduce the evaporation of metals at said stage and thus reduce particle emission and to obtain an improved recycling efficiency.

During the process of the present invention it is desirable to control parameters such as temperature of primary heat treatment and of halogenation, mass flow to, from and in the primary heat treatment chamber and halogenator in order to achieve higher efficiency. Thus, the waste movement into and in the primary heat treatment chamber may be adjusted in order to improve evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material and reduction of metal oxides and mechanical reduction of the waste. The temperatures in the primary heat treatment chamber may be adjusted in order to obtain more efficient reaction with carbon, and its diffusion; the waste movement in the halogenator may be adjusted in order to achieve more efficient halogenation; the air flow in the primary heat treatment chamber may be adjusted in order to achieve an optimal carbonization, organic destruction, cracking, metal oxide reduction and halogenation. The chlorination chamber temperature may be adjusted in order to evaporate material having low boiling point or sublimation point and later material having higher boiling point or sublimation point, thus performing separation thereof.

Furthermore, the air flow in to the primary heat treatment chamber may be regulated in order to produce carbon in quantities required for optimal halogenation.

An advantage of carbonization resulting in incomplete combustion over that resulting in complete combustion is that the former results in less gasses than the latter, most of the organic matter is cracked into carbon and hydrogen molecules, the formation of CO and CO_2 molecules is substantially reduced. The gas flow in incomplete combustion is reduced in temperature, volume and velocity, which substantially reduces the particle emission and simplifies the treatment of the flu gas which consists of heat exchanging, heat recovery and emission control. The lower temperature reduces the amount of volatile inorganic matter in the flu gas. The lower velocity of the gas flow reduces the amount of particles drawn. The substantial reduction of in-flow of air usually required for said ~~incomplete combustion can reduce the amount of emitted flu~~ gas. The volatile organic matter only, can be further incinerated in the secondary chamber, however, said gas will require less oxygen for its incineration and will be almost free of non-gaseous particles. All the above renders the system more environmental friendly especially regarding the “greenhouse effect”.

In the event that any of the various fractions of the metal halides which were deposited in the fractional deposition contains a mixture of halides, said mixture may be further separated and purified by known hydrometalurgy technologies and by further fractional deposition of higher resolution.

Most of the waste is recycled by decomposing the material to its basic elements or their halide / oxide derivatives.

The process of the present invention being self-catalyzed, requires little or no addition of material for the purpose of catalysis. According to the present invention, use as catalysts in the recycling phase, is made of elements which exist in most of the wastes to be treated, thus the introduction of catalysts *per se* to the process is minimized.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 schematically illustrates an apparatus for a high efficient process for the treatment of multi-element wastes according to the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

According to one embodiment of the present invention, the scrap to be treated is inserted to a shredder, 1, and shredded therein. The shredded

scrap is loaded by means of a ram loader, 2, into the rotary heat treatment chamber, 3, and the primary heat treatment is performed therein. The gaseous material exiting the primary heat treatment chamber flows to the secondary combustion chamber, 5, where all matters are combusted at an elevated temperature. Additional air is introduced through regulated vent (17). The hot flu gas flows to the heat exchanger (8) into which water is introduced through conduit (7) and withdrawn as a hot stream through conduit (18). The chilled flu gas passes through scrubber (6), where any gaseous emission is absorbed by caustic or lime. The flu gas further passes through the filter bag (4), to remove any particles. The filtered flu gas is released to the atmosphere by means of blower (19), through stack (20). The formation of high pressure within the system is prevented by means of valve (17) and blower (19). The non-gaseous material remaining from the primary heat treatment is introduced into the halogenation chamber, 9, through valve, 21, which is closed during the halogenation reaction. Halogen compounds such as chlorine, bromine or a mixture thereof are introduced to the halogenation chamber via conduit 10. Condensation columns 11, 12, 13, 14 and 15 are maintained accurately at temperatures T_1, T_2, T_3, T_4 and T_5, accordingly, under the condition that $T_1>T_2>T_3>T_4>T_5$, and at an accurately controlled pressure. The gaseous product of the halogenation reaction is passed through said condensation columns, and the metal halides deposit thereon according to their characterized deposition temperature, and are collected and thus separated. The

remaining gas which comprises excess halogen gas exits the apparatus through conduit 16. The non-gaseous material which remained in the halogenation chamber is collected and separated if required. Said remaining gas of the halogenation reaction may be recycled back into the halogenation chamber.

According to a preferred embodiment of the present invention metal scrap/waste is reduced to a size that can be introduced to the equipment. Organic waste is treated in a controlled atmosphere or in a molten metallic phase with an oxygen deficiency in order to maintain carbon particles which will serve as catalysts and also reduce the oxide layer on the metallic waste. The gas streams pass through an air-controlled abatement system. The heated inorganic waste and carbon is then fed to a halogenation reactor either - vertical, horizontal, fixed or fluidized bed. Additional carbon is introduced if needed. The carbon residue from the incineration process is used as a catalyst for the halogenation process.

According to a preferred embodiment, most of the metallic scrap is oxidized after a certain time of being exposed to the air, humidity and sun. This causes a problem to the extent that the oxide layer acts as a passive layer which deactivates the chlorination process. Said problem can be solved according to the present invention by the controlled incineration with oxygen deficiency at elevated temperatures of between 300°C and

1050°C, preferably between 800°C and 850°C. Thus, in the presence of a sufficient amount of carbon in the incinerator, the metal oxides and carbon may be converted to metals and CO and CO_2 according to the following empirical formula:

$$M_xO_y + C \dashrightarrow M + CO + CO_2$$

According to a preferred embodiment the hot gas from secondary combustion chamber may pass through a heat recovery system namely a waste heat boiler, in which the energy is converted into steam and may produce electrical energy.

According to a preferred embodiment, use is made of bromine and/or bromine derivatives to accelerate chlorination of metals, especially noble metals.

According to one preferred embodiment, a portion of the flu gas exiting the primary heat treatment chamber or a portion of the flu gas exiting the secondary heat chamber are introduced to the halogenation chamber. Thus, oxygen or catalysts such as SO_x, NO_x and/or carbon compounds, may be recycled.

According to a preferred embodiment of the present invention, the gas flow resulting subsequent to the fractional deposition process, which contains a high percentage of halogen gas, may be recycled back into the halogenator.

EXAMPLES

Example 1

500 Grams of unsorted automobile scrap was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a length of approximately 10mm. Said pieces were carbonized (in the absence of oxygen) at a temperature of between 600°C-700°C for about 1 hour. Table 1 shows the content of said scrap before and after carbonization.

NAME	ELEMENT CONTENT (wt%)										
	Fe	Al	Cu	Ni	Mg	Co	Sn	O	Organic	noble metal	Wgt	%
Scrap before carbonization	53	18	4	2	4	1.5	1.3	5	11	0.05	500	100
Scrap after carbonization	61	21	4.5	2.0	4.6	1.7	1.5	-	2.4 carbon	0.05	432	86.4

Table 1

The carbonized material was further chlorinated at a temperature of about 750°C for 3 hours, and the various metal chlorides were separated. Table 2 shows the content of the material after the chlorination reaction .

ELEMENT CONTENT (%)										
Weight (gr.)	$FeCl_3$	$AlCl_3$	$SnCl_4$	NiCl	CuCl	$CoCl_2$	noble metal	$MgCl_2$	Conden. Chamber	Conden. Temp(°C)
	771			0.18					II	250-300
		440							III	1000
			14.2						IV	50
				14.5					I	600
130	4.26			3.5	28.5	15	0.46	78.3	V	
total: 1370	775.26	440	14.2	18.18	28.5	15	0.46	78.3		

Table 2

Example 2

600 Grams of crushing electronic scrap was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a length of approximately 10mm. Said pieces were carbonized (in the absence of oxygen) at a temperature of between 650°C-700°C for about one hour. Table 3 shows the content of said scrap before and after carbonization.

	Cont. Element %												
NAME	Fe	Cu	Ni	Sn	Pb	Zn	Co	Au	Ag	Pd	O	Organic	C	Wt
Scrap before Carbonization	6	20	2.5	5.0	2.0	3.0	0.25	0.025	0.15	0.018	6	56	-	600
Scrap after Carbonization	13	44	5	11	4.4	6.6	0.5	0.055	0.33	0.04	-	2.5	4.0	270

Table 3

The material treated by means of primary heat treatment was chlorinated at a temperature of about 250°C for about 3 hours, and the various metal

chlorides were separated. Table 4 shows the content of the material after the chlorination reaction.

NAME	Wgt.	$FeCl_3$	$SnCl_4$	$NiCl_2$	$ZnCl_2$	$CoCl_2$	CuCl	$PlCl_2$	AuCl g/t	Ag g/t	Pd
Chloride iron $FeCl_3$		101									
Chloride Tin $SnCl_4$			61.0								
Chloride Nickel $NiCl_2$				23							
Chloride Zinc $ZnCl_2$					32						
Residue in Chlorinator	198			5.0	3.5	2.7	173	14.2	0.061%	0.17%	0.058%
Total	415	101	61.0	28	35.5	2.7	173	14.2			

Table 4

Example 3

200 Grams of mixture of spent catalyst waste were introduced to the process of the present invention as follows: Said waste was treated by means of primary heat treatment, in the absence of oxygen, at a temperature of about 650°C for about 1.5 hours. Table 5 shows the content of said waste before and after primary heat treatment.

NAME	Cont. element %								
	Weight total	WO_2	Ta_2O_5	TiO_2	Co_2O_3	Organic	C	SiO2	Al_2O_3
Scrap before Calcination	200 gr	38	9	31.0	3.5	20	-	24	14
Scrap after Primary heat treatment	100	W 31	Ta 7	31.0	Co 2.2	-	4.5	16	8

Table 5

100 Grams of the calcinated material were chlorinated at a temperature of about 700°C, for about 2 hours, and the various metal chlorides were separated. Table 6 shows the content of the material after the chlorination reaction.

NAME	Weight	WCl_6	$TaCl_5$	$TiCl_4$	$CoCl_2$	SiO_2	Al_2O_3	Condens. Temp (°C)
Tungsten Chloride		64						200-250
Tantalum Chloride			9.0					200-250
Titanium Chloride				122				0-20
Residue in Chlorinator	25.0				4.6	14	6.8	500
Total	245	64	9.0	122	4.6	14	6.8	

Table 6

The remaining residue in the chlorinator was treated by separating $CoCl_2$ from SiO_2 and AlO_3, e.g. according to the principle of differences of solubility in water as described in the following equation:

$$CoCl_2 + SiO_2 + Al_2O_3 + H_2O \dashrightarrow H_2O\,(Co^{++} + 2Cl^{-})_{aq} + SiO_{2\,(solid)} + Al_2O_{3\,(solid)}$$

The remaining SiO_2 and AlO_3 were introduced to a chlorination chamber at 900°C and were converted to $AlCl_3$ (18g) and $SiCl_4$ (32g).

Example 4

The primary heat treatment of Example 3 was repeated, and 100g of the material treated by means of primary heat treatment was chlorinated at a temperature of about 900°C, for about 1.5 hours, and the various metal chlorides were separated. Table 7 shows the content of the material after the chlorination reaction.

NAME	Weight	$CoCl_2$	WCl_6	$TaCl_5$	$AlCl_3$	$TiCl_4$	$SiCl_4$
Chloride Cobalt - $CoCl_2$		4.7					
Chloride Tungsten - WCl_6			64				
Chloride Tantalum - $TaCl_5$				9.0			
Chloride Aluminum - $AlCl_3$.					18		
Chloride Titanium - $TiCl_4$						122	
Chloride Silicon - $SiCl_4$							32
Residue	6.0				Al_2O_3 2.5		SiO_2 3.5

Table 7

Example 5

A mixture of 100g of Nickel-Cadmium batteries was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a length of approximately 1-5cm. Said pieces were calcinated (in the absence of oxygen) at a temperature of about 650°C, for about 3 hours. Table 8 shows the content of said scrap before and after primary heat treatment.

Type of scrap	% Ni	%Cd	%Fe	% Organic Silicon
Before Primary heat treatment	20	14	32	34
After Primary heat treatment	24	16	34	SiO_2 - 16; C - 20

Table 8

The material treated by means of primary heat treatment was chlorinated at a temperature of about 650°C, for about 1.5 hours, and the various metal chlorides were separated. Table 9 shows the content of the material after the chlorination reaction.

NAME	Weight	$FeCl_3$	$NiCl_2$	$CdCl_2$	SiO_2	C
Chloride Iron $FeCl_3$		96				
Chloride Nickel $NiCl_2$						
Chloride Cadmium $CdCl_2$						
Residue in Chlorinator	101		49	26	16	10

Table 9

While some embodiments of the invention have been illustrated, it will be clear that the invention may be carried out by persons skilled in the art with many modifications, variations and adaptations, without departing from its spirit or exceeding the scope of the claims. Thus, e.g., the invention may be applied to scrap or apparatus different from that herein described.

CLAIMS

1) A high efficient recovery process for the treatment of multi-element waste which comprises the steps of:

a) heat treatment of the waste in the presence of a controlled amount of oxygen;

b) halogenation of the product of step "a"; and

c) separation of the metal halide products of step "b".

2) A process according to claim 1 in which said multi-element waste is unsorted.

3) A process according to claim 1 in which the waste to be recovered is such that has been mechanically prepared in a process which includes any one or more of the steps of shredding, crushing, milling and briquetting.

4) A process according to claim 1 in which said primary heat treatment further comprises mechanically agitating the waste during said treatment.

5) A process according to claim 1 in which the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material,

carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

6) A process according to claim 1 in which the halogenation reaction therein is selected from the group which consists of chlorination, bromination, or chlorination and bromination.

7) A process according to claim 1 in which at least a portion of the heat energy afforded in the primary heat treatment is used in the halogenation reaction.

8) A process according to claim 1 in which at least a portion of the product of the primary heat treatment is used as a catalyst in the halogenation reaction.

9) A process according to claim 8 in which said products to be used as catalysts are selected from the group which consists of carbon, bromine, carbon, CO, CO_2 and SO_x and NO_x compounds.

10) A process according to claim 1 wherein the primary heat treatment is performed in an oven.

11) A process according to claim 10 wherein said oven is at a temperature of less than about 1000°C.

12) A process according to claim 1 wherein the primary heat treatment is performed in a metallic molten bath.

13) A process according to claim 12 wherein said molten bath is at a temperature of between 500°C and 1600°C.

14) A process according to claim 1 which further comprises a secondary heat treatment comprising heating the gaseous flow which results from the primary heat treatment to a temperature of more than 1200°C.

15) A process according to claim 1 in which said halogenation step further comprises mechanically agitating the waste during said step.

16) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between 150°C and 1500°C.

17) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between 700°C and 750°C.

18) A process according to claim 1 in which the waste comprises a substantial percentage of any of the metals selected from the group which consists of Ag, Pt and Pd, and the halogenation reaction is performed by using a mixture of bromine and chlorine.

19) A process according to claim 18 in which said mixture of chlorine and bromine comprises between 93% and 99% chlorine and the remainder is bromine.

20) A process according to claim 1 in which at least a portion of the excess halogen gas remaining from the halogenation reaction is recycled back to the halogenation chamber.

21) A process according to claim 1 in which the separation of the metal halides is by means of any one or more of the group selected of gaseous or liquid fractional deposition, distillation, fractional distillation, filtration, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution and selective extraction.

22) An apparatus for a high efficient recovery process for the treatment of multi-element wastes, which comprises a primary heat treatment chamber, a halogenation chamber and a separation unit; said primary heat treatment chamber comprises a waste inlet, a flu-gas outlet and

means of heating; said halogenation chamber comprises a means of heating, a halogen compound inlet and an outlet;

23) An apparatus according to claim 22 in which the flu-gas outlet of said primary heat treatment chamber is connected to said halogenation chamber by means of a conduit, which comprises a valve.

24) An apparatus according to claim 22 in which said separation system comprises one or more of the units selected from the group which consists of fractional deposition unit, distiller, filter, settler, selective oxidation chamber, selective halogenation, chamber evaporation chamber and selective dissolution unit or any combination thereof;

25) An apparatus according to claim 24 in which said separating unit is in contact with the outlet of said halogenator by means of a conduit.

26) An apparatus according to claim 22 in which said separation system is a gaseous fractional deposition system; the inlet of which is connected to the outlet of said halogenator, by means of a conduit.

27) An apparatus according to claim 26 in which the outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber, and said pipe comprises a one-way valve in the

30) An apparatus according to claim 29 in which said filter is selected from the group which consists of fabric filter, electroststic filter, and high temperature filter.

31) An apparatus according to claim 22 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill and briquetter which are connected to the primary heat treatment chamber; providing that the outlet of the unit connected to the primary heat treatment chamber is connected to the inlet of said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

32) An apparatus according to claim 22 which further comprises any one or more of the units selected from the group which consists of shredder, ~~crusher, mill and briquetter which are connected between the primary~~ heat treatment chamber and the halogenation chamber; providing that the outlet of the unit which is connected to the halogenation chamber is connected to the inlet of said halogenation chamber by means of a conduit; further providing that the outlet of the primary heat treatment chamber is connected to the inlet of the unit which is connected to said primary heat treatment chamber by means of a conduit; further

providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

33) An apparatus according to claim 22 in which said primary heat treatment chamber further comprises a means of agitating material.

34) An apparatus according to claim 33, in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid and walking grid.

35) An apparatus according to claim 22 in which said halogenation chamber further comprises a means of agitating material.

36) An apparatus according to claim 35, in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid and walking grid.

37) An apparatus according to claim 22 in which the primary heat treatment chamber is placed horizontally, vertically or in any other advantageous angle.

38) An apparatus according to claim 22 in which the halogenation chamber is placed horizontally, vertically or in any other advantageous angle.

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LUZZATTO & LUZZATTO
By ע"י

4519/97
Ariel ROSENBERG

One Sheet of Drawings

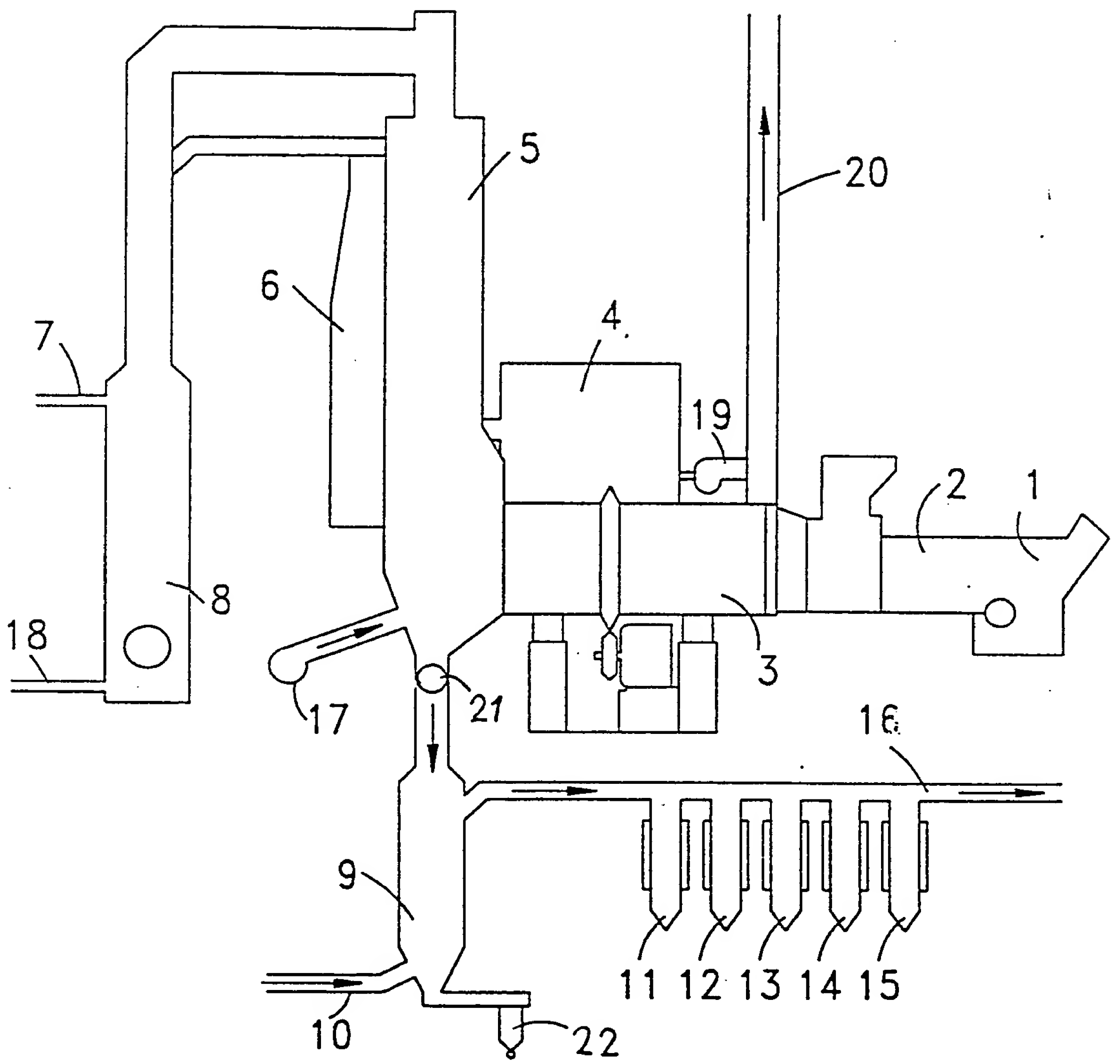

Fig. 1